PART I. THE SECONDARY BAND IN THE ULTRAVIOLET ABSORPTION SPECTRA OF ACETOPHENONES AND RELATED COMPOUNDS.

PART II. THE STUDY OF HYDROGEN BONDING AND SIMILAR EFFECTS BY MEANS OF ULTRAVIOLET ABSORPTION SPECTRA.

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A THESIS

by

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ABSTRACT

The absorption spectra of some acetophenones and benzoic acids have been measured in different solvents in the region 200-400 mμ. The two major bands are compared and it is found that interactions which considerably alter the high intensity band have less and somewhat different effects on the secondary band. Solvent effects and the changes observed on substitution indicate that the weaker band (C-band) is essentially of similar character as the high intensity primary band (B-band). A unifying hypothesis to account for the observed changes is presented.

PART I. THE SECONDARY BAND IN THE ULTRAVIOLET ABSORPTION SPECTRA OF ACETOPHENONES AND RELATED COMPOUNDS.

INTRODUCTION

It has previously been stated that steric effects in the B-band of the acetophenone series can be classified into three types.[1,2,3,4] These are as follows: (1) slight effects, giving rise to intensity changes only (2) larger steric effects giving both wavelength and intensity changes, and (3) larger steric effects, causing the molecule to absorb as two distinct entities. Generally it was found that the location of maximal absorption of the B-band depended primarily on the steric and mesomeric (resonance) effects of the substituents.[3,5] This thesis is intended to examine the secondary band in this region, and to present a consistent explanation in terms of electrical and steric effects for the changes observed in this band.

The secondary band will be referred to as the C-band, following the nomenclature adopted by Moser and Kohlenberg,[6] who also named the main absorption band the B-band. This alphabetical order assigns the letters A, B and C to the bands as they are normally found proceeding from about 200 mμ to longer wavelength.

1. Forbes, W.F. and Mueller, W.A. Can. J. Chem. 33:1145. 1955.
2. Forbes, W.F. and Mueller, W.A. Can. J. Chem. 34:1340. 1956.
3. Forbes, W.F. and Mueller, W.A. Can. J. Chem. 35. In Press.
4. Braude, E.A. and Sondheimer, F. J. Chem. Soc. 3754. 1955.
5. Forbes, W.F. and Ralph, A.S. Can. J. Chem. 34:1447. 1956.
6. Moser, C.M. and Kohlenberg, A.I. J. Chem. Soc. 804. 1951.

Other designations have been proposed for this C-band, which has also been referred to as the secondary band,[7] because the band is of much smaller intensity and therefore in a sense "secondary"; or as the B-band[8] to indicate its association with "benzene". This latter designation receives support since the symmetry assignment of the excited state is most probably B_{2u}.[9]

THE C-BAND IN ULTRAVIOLET ABSORPTION SPECTRA

The C-band of the compounds listed in Table I is ascribed to transitions involving the benzene ring, since similar bands are found in phenols, aniline, and in a large number of other benzenoid compounds, as well as in benzene itself.[7] In most cases the intensity of absorption of the C-band is considerably smaller than the absorption intensity of the B-band. For benzene the C-band is located at approximately 260 mμ, $\varepsilon = 250$. For mono-substituted benzene derivatives, both B- and C-bands are displaced to longer wavelengths and often maintain, regardless of the degree of displacement, a relatively regular wavelength relationship. (Doub and Vandenbelt[7] report the spectra of thirteen mono-substituted benzene derivatives where the ratio of the maximal wavelengths $\lambda_{\text{C-band}} / \lambda_{\text{B-band}}$ is consistently 1.23 ± 0.05). Exceptions are nitrobenzene, and to a lesser degree acetophenone and benzaldehyde, where the wavelength ratios are different.

7. Doub, L. and Vandenbelt, J.M. J.Am. Chem. Soc. 69:2714. 1947.
8. Braude, E.A. Ann. Reps. Chem. Soc. 42:105. 1945.
9. Forbes, W.F. and Mueller, W.A. Can. J. Chem. 34:1347. 1956.

Displacements to longer wavelength are accompanied by increased absorption intensities, but the absorption increments in the C-band show only slight similarities to the absorption increments observed in the B-band on bathochromic displacement. The main dissimilarities are: firstly, NH_2-, OH-, and OMe- groups in the C-band produce more marked intensity increments than, for instance, alkyl groups or halogens. Secondly, intensity changes for mono-halogen substituted benzenes are in the reverse order (Bowden and Braude[9,10] for solution spectra report an order F>Br>Cl) to wavelength shifts in the B-bands.[5] This apparent dependence of intensities on inductive effects for mono-substituted benzenes has received a theoretical interpretation from molecular orbital theory calculations.[10] The further generalisation that absorption intensities and frequencies depend primarily on inductive and mesomeric effects respectively,[10] is however, too over-simplified even for the C-band.

A number of points arising out of these observations may be noted. In the first place, the molecular orbital treatment as described by Matsen and co-workers,[10,11] while providing a satisfactory semi-quantitative interpretation of the intensities of mono-substituted benzenes, does not readily lend itself to the interpretation of the di-substituted derivatives (cf. also the

10. Robertson, W.W. and Matsen, F.A. J. Am. Chem. Soc. 72:5252. 1950.
11. Matsen, F.A . J. Am. Chem. Soc. 72:5243. 1950.

"Discussion" below). Secondly, the "anomalous" nature of some of the spectra of iodine-substituted compounds may be noted (see Table I). This may be because of steric factors,[5] and requires further elucidation. Thirdly, the possible significance of inductive effects in the C-band suggests examination of para-disubstituted compounds, where any inductive interaction of the two substituents on each other would be small.

The data for the C-band of para-disubstituted compounds indicate a different type of interaction from that observed in the B-band. Since the C-band of many para-disubstituted compounds resemble one, or are intermediate with respect to both the mono-substituted parent compounds, this indicates that both inductive and mesomeric interactions are small (cf. for example, in Table I the C-band of the following groups of compounds: 4-chloroacetophenone and acetophenone; 4-fluoroacetophenone, acetophenone and fluoro-benzene; 4-chlorobenzoic acid and benzoic acid). Exceptions arise (cf. for example phenol and p-cresol),[12] where the introduction of a para-substituent gives rise to approximately equal bathochromic shifts and absorption increments in both B- and C-bands; these will be referred to again later.

In the meantime it may be noted that this, generally different, interaction in the two bands of para-disubstituted compounds is of some practical importance. For example, it accounts for the

12. Friedel, R.A. and Orchin, M. Ultraviolet Spectra of Organic Compounds. John Wiley and Sons, Inc., New York. 1951.

observation that the C-band in para-isomers is frequently obscured by the considerably displaced and intensified B-band. Thus, the band in the 320-360 mμ region for aminoacetophenones and aminobenzoic acids may be assumed to be a C-band because this band is covered in the para-isomers and therefore no great displacement towards longer wavelength and absorption increase takes place. This assignment is in contrast to the one favoured by Klevens and Platt,[13] who regard the 257 mμ band in dimethylaniline as the C-band. This interpretation in agreement with Bowden and Braude[9] would be to regard this band as the analogue of the 235 mμ band (B-band) in aniline.

Turning to meta-disubstituted compounds, it may be noted that the C-band only occasionally resembles the C-band of one of the mono-substituted analogues; more frequently there is some evidence for interaction particularly for the hydroxy, methoxy, and aniline derivatives of the compounds studied (see Table I). This interaction becomes increasingly important for the C-band of ortho-disubstituted derivatives. Using the meta-disubstituted isomer as the reference compound, the interaction may be divided into at least two groups; compounds in which a hypsochromic shift and loss of absorption intensity is observed (for example, 2-chloroacetophenone) and compounds for which a distinct bathochromic shift with enhanced absorption intensity is observed (for example, 2-hydroxyacetophenone).

13. Klevens, H.B. and Platt, J.R. J. Am. Chem. Soc. 71:1714. 1949.

At this point, the choice of reference compound used for comparing these (ortho-effects) requires discussion. For the B-band it was shown[2] that the para-isomer is the most satisfactory reference compound. For the C-band, by contrast, the para-isomer is less suitable as a reference compound because para- and ortho-isomers, even in the absence of steric effects, do not give rise to similar C-bands. (The wavelength shifts may conceivably be comparable, but the intensities are certainly not as may be noted from Table I). Furthermore the para-isomer would make an unsatisfactory reference compound, since the C-band is there often submerged by the displaced B-band (see above). Hence the choice lies between the C-band of the meta-isomer and the C-band of one of the mono-substituted parent compounds, and both will be made use of in the discussion. Neither of them is entirely satisfactory; the meta-isomer has the advantage that frequently there is a resemblance between ortho- and meta-isomers. The mono-substituted parent compound may be of interest since there are indications that for the B-band the spectrum[2] of the mono-substituted compound often resembles both the ortho- and meta-disubstituted compounds. This may also be true for the C-band.

Returning now to the main theme, it is evident from Table I that ortho-effects in the C-band differ from ortho-effects as observed in B-bands. In the ortho-substituted compounds listed in Table I the C-bands are well defined, even if both ortho-positions are occupied. The C-bands are all displaced towards the visible when compared to the

C-band of acetophenone or benzoic acid respectively, and this bathochromic shift is in the order NH_2> OH > OMe > Br > Cl (compared to the meta-disubstituted isomer, as has been noted above, either a hypsochromic or bathochromic shift is observed). This order is the same as the order of bathochromic shifts in the B-band for para-substituted acetophenones or benzoic acids, and may be correlated with the ability of the substituents to release unshared electrons. Further, the fact emerges that the C-band apparently never completely disappears in ortho-disubstituted compounds, and this indicates that conjugation between the two entities still takes place; actually for many of these disubstituted compounds the C-band is enhanced with respect to either the mono-substituted or the mono-ortho-substituted compound. (See Table I)

STERIC EFFECTS AND AN INTERPRETATION OF THE CHANGES OBSERVED ON SUBSTITUTION

Previous explanations concerning steric effects in the C-band vary. Moser and Kohlenberg[6], for example, state that steric interactions between the carboxyl group and another atom or group in ortho-substituted benzoic acids apparently have no effect upon this band. Cram and Cranz[14] have also discussed this band and conclude that the C-band is particularly sensitive to transitions associated with ortho-resonance forms.

The hypothesis presented in this thesis to explain why steric inhibition of resonance has a marked effect upon the B-band but apparently none or quite a different effect on the C-band, is based on

14. Cram, D.J. and Cranz, F.W. J. Am. Chem. Soc. 72:595. 1950.

the following assumptions: (1) the electronic excitation leading to the C-band involves transitions which require more energy at the energetically most favourable interplanar angle of the ground state; (2) this ground state attains a minimum at an interplanar angle of about 90 degrees, because there is then a secondary maximum of interaction between the π-electrons of the benzene ring and some of the p-electrons of a substituent. These assumptions are illustrated in Figure I.

Applying the hypothesis it is noted that in contrast to the B-band, the C-band is comparatively insensitive to smaller steric effects. An example of this is provided by ortho-methyl derivatives, such as 2-methylacetophenone, where the intensity of the B-band is approximately halved while the C-band shows no such change (see Table). Intensity losses of this type in the B-band have been ascribed to the excited state because of its different energy relationship with respect to interplanar angles - no longer participating in some of the transitions which lead to the observed absorption intensity of a planar reference compound[3,9]. In the C-band, since the electronic excited state is assumed to be different, no such restriction is observed.

In the example cited (2-methylacetophenone) there will, however, be a change in the C-band, since, as transitions leading to a B-band become less probable because of the increased angle of twist in the ground state, this same increased angle of twist will make transitions more probable, as indicated by arrows "C" in Figure I.

TABLE I

ABSORPTION SPECTRA OF SUBSTITUTED ACETOPHENONES AND BENZOIC ACIDS

Wavelengths and intensities of the B- and C-bands (in this and subsequent tables underlined figures represent inflections)

	ACETOPHENONES								BENZOIC ACIDS							
	Absolute or 95% Ethanol				Cyclohexane or Ether				Absolute or 95% Ethanol				Cyclohexane or Ether			
	B-band		C-band		B-band		C-band		B-band		C-band		B-band		C-band	
Substituent	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}
None	240	12,500[1]	276	1000[1]	239	12,600[4]	275	810[4]	227	11,000[2]	271 279	760[3] 550	230	10,000[4]	275 280	750[4] 760
			(Toluene		207	9500	262	300	207	9300	260	300)				
2-Methyl-	242	8500[1]	283	1250[1]					228	5000[2]	279	725[3]				
3-Methyl-									232	9000[2]	279	1000[3]				
4-Methyl-	252	15,000[1]	278	850[1]					236	14,000[2]	-	-[3]				
2,6-Dimethyl-	251	5600[5]	281 ca.290	890[5] 740					-	-[3]	270	725[3]				
			(Fluorobenzene (in ethanol]						204	6200[3]	254	900[6])				
2-Fluoro-	236	10,000	280	1550	233	9500	279	1600	223	9500[2]	273 ca.280	1620 1300	225-226	10,500	276 ca.284	2000 1600
3-Fluoro-	236	10,500	281 289	1700 1250	2 35	9500	280 290	1700 1250	225	10,000[2]	274 281	1700 1400	228	11,000[7]	277 285	1900 1700
4-Fluoro-	242	11,500	-	-	240	12,000	266	850	228	11,000[2]	262 268	500 300	230	12,600[7]	263 269	650 400
			(Chlorobenzene [in ethanol]						210	7500[6]	257	170[6])				
2-Chloro-	238	5500	281	750	235	5700	280	650	ca.229	5000[2]	278	760[3]			280	1000[4]
3-Chloro-	240	10,000	286	1050	239	10,000	286 295	1100 900	230	8500[2]	284	950[3]				
4-Chloro-	249	16,000	ca.286	650	249	17,000	272 284	900 500	234	15,000[2]	-	-[3]	237	15,100[4]	275	730[4]
2,6-Dichloro-									-	-[3]	264 274	440 500				
			(Bromobenzene [in ethanol]						210	8600[6]	261	200[6])				
2-Bromo-	236	4900	282	780	236	4900	282	700	ca.224	6500[2]	262 282	560[3] 760			282	1050[4]
3-Bromo-	240	9500	287 ca.293	1050 950	240 ca.245	10,000 8000	ca.282 287 296	900 1100 950	ca.225	8500[2]	280	830[3]			284	1100[4]
4-Bromo-	253	16,000	ca.286	900	253	19,500	ca.286	600	238.5	16,000[2]	-	-[3]	242	16,100[4]	ca.270	800[4]
2,6-Dibromo-									-	-[3]	262 272	930[3] 870				
			(Iodobenzene [in ethanol]						226	13,000[6]	256	800[6])				

3-Chloro-	240	10,000	286	1050	239	10,000	286 295	1100 900	230	8500[2]	284	950[3]				
4-Chloro-	249	16,000	ca.286	650	249	17,000	272 284	900 500	234	15,000[2]	-	-[3]	237	15,100[4]	275	730[4]
2,6-Dichloro-									-	-[3]	264 274	440 500				
(Bromobenzene [in ethanol]									210	8600[6]	261	200[6])				
2-Bromo-	236	4900	282	780	236	4900	282	700	ca.224	6500[2]	262 282	560[3] 760			282	1050[4]
3-Bromo-	240	9500	287 ca.293	1050 950	240 ca.245	10,000 8000	ca.282 287 296	900 1100 950	ca.225	8500[2]	280	830[3]			284	1100[4]
4-Bromo-	253	16,000	ca.286	900	253	19,500	ca.286	600	238.5	16,000[2]	-	-[3]	242	16,100[4]	ca.270	800[4]
2,6-Dibromo-									-	-[3]	262 272	930[3] 870				
(Iodobenzene [in ethanol]									226	13,000[6]	256	800[6])				
2-Iodo-									ca. 233	7000[2]	285	1450	ca.232 ca.240 ca.247	8500 7000 4500	286	1600
3-Iodo-	ca.250	7100	295	1040	ca.246 ca.250	6800 6000	292 300	1050 930			284 290	950 900	ca.233	9800	283 291	1000 900
4-Iodo-	262	16,000	-	-	263	19,500			252	17,000[2]	ca.282	1700	252	18,500	ca.282	1350
(Phenol					210	6000[7]	263 269 276	1400[7] 2200 2100	218.5	6000	271	1900)				
2-Hydroxy-					251	9700[4]	327	3800[4]	236	7500[2]	307	3700[3]	237	7800[4]	307	4400[4]
3-Hydroxy-					246	8900[4]	306	2900[4]	236	6000[2]	301	2200[3]	234	6600[4]	296	2900[4]
4-Hydroxy-					267	19,100[4]	-	-[4]	251	12,500[2]	-	-[3]	251	18,300[4]	-	-[4]
2,6-Dihydroxy-									-	-[3]	277 311	1950[3] 3500				
(Anisole [in hexane])																
2-Methoxy-					246	8000[4]	306	2600[4]	230	6000[2]	291	2700[3]			291	3500[4]
3-Methoxy-					246	8500[4]	304	2800[4]	230	7000[2]	293	2450[3]	234	7000[4]	295	2500[4]
4-Methoxy-					266	18,000[4]	-	-[4]	249	14,000[2]	-	-[3]	251	18,300[4]	-	-[4]
2,6-Dimethoxy-									-	-[3]	282	1850[3]				
(Aniline					233	9000[7]	286	1800[7]	234	1700[7]	284	800[7])				
2-Amino-	254	5600	359	4350	252	5500	347	4350	247	6500	332	4500	252	7400[4]	333	5200[4]
3-Amino-	ca. 255	7000	338	1900	ca.246	9000	320	2500	ca.241	7000[7]	319	2100	244	7800[4]	320	2800[4]
4-Amino-	316	20,000	-	-	285	19,000	-	-	288	18,500	-	-	277	20,600[4]	-	-[4]
(Nitrobenzene					252	9000	ca.285	1500	257	8000	-	-)				
2-Nitro-	257	6000	-	-	254	6000	-	-	ca.255	3500[2]						
3-Nitro-	ca.260	6500	ca.300	800	ca.254	7000	ca.288 298	1100 750	255	7000[7]						
4-Nitro-	261	14,000	ca.298 ca.312	2200 1200	ca.258	14,000	ca.292 ca.308	2000 1000	258	12,000	ca.284	2500	255	13,000	ca.294	2000

[1](1); [2](19); [3](6); [4](36); [5](4); [6](26); [7](This band is concentration dependent).

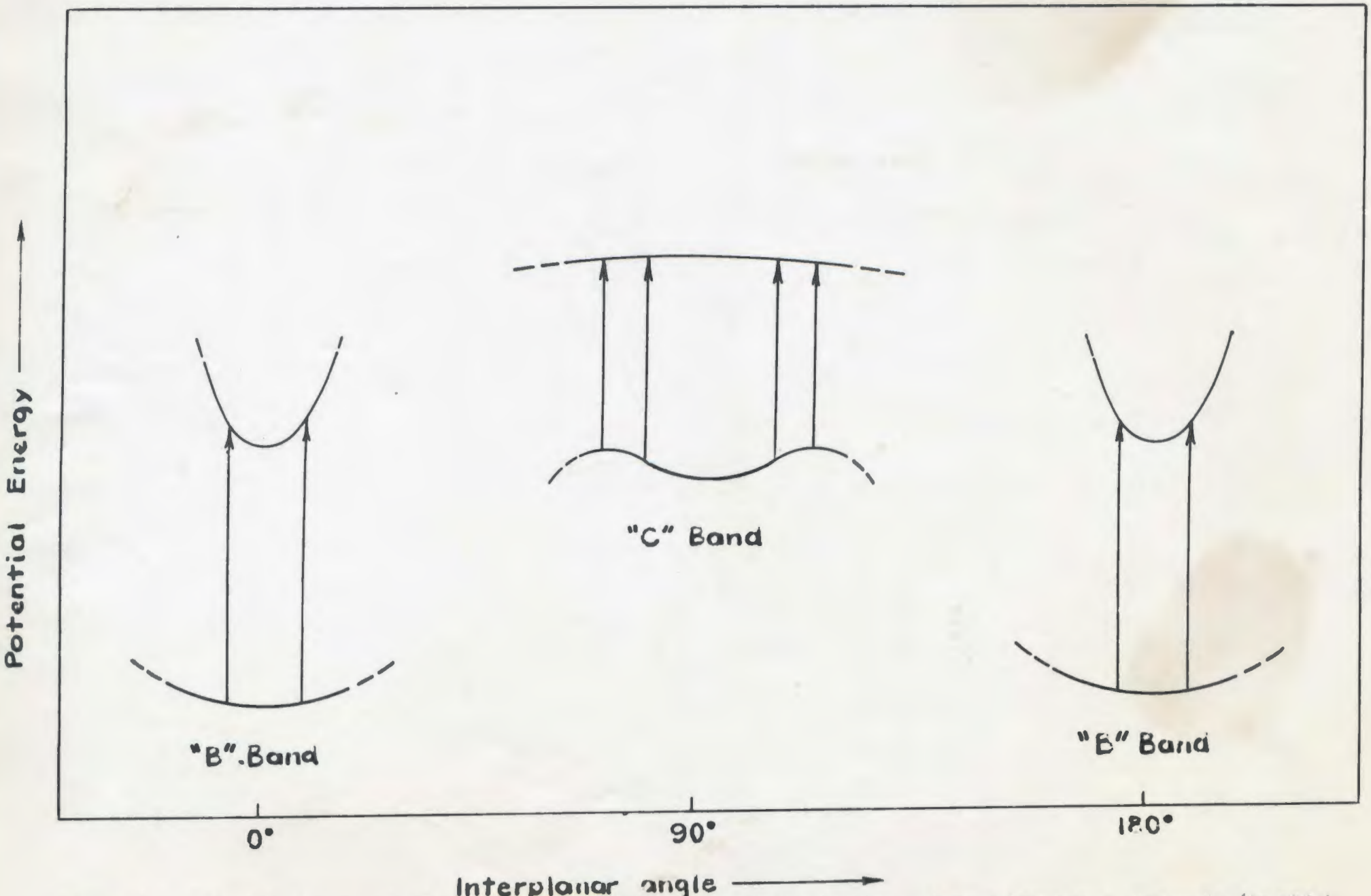


Figure 1. Schematic representation of the potential energy of electronic states in benzenoid compounds (in which steric interactions between substituents are assumed small) as a function of twist about the single bond joining the benzene ring to the acyl group. The vertical arrows "B" and "C" represent the transitions leading to the B- and C- bands respectively.

Hence a slight bathochromic shift accompanied by increased absorption intensity is observed (cf. Table 1). This effect is considerably enhanced in compounds like 4-acetyl-hydrindacene (λ_{max} 308 mμ, ε = 3000[1]), where both planar forms are subject to steric interaction.

The hypothesis also accounts for the observation that even in considerably hindered compounds where the interplanar angle is quite large,[9,15] the C-band still absorbs with appreciable intensity. This follows since conjugation is still possible in the ground state, although transitions leading to the B-band no longer occur. It is of interest in this connection that the carbonyl stretching frequencies of hindered acetophenones support the hypothesis of appreciable residual conjugation in the ground state.[3] Conjugation, however, is only residual and hence the molecule will also absorb as two distinct entities. This may be taken to account for the eventual reduced absorption intensity even in the C-band.

Next, for OH-, OMe-, and NH_2- substituents, a pronounced bathochromic shift is observed, accompanied by increased absorption intensity. For this observation the hypothesis again provides an answer, since OH-, OMe-, and NH_2- substituents all contain unshared p-electrons. This gives rise to interaction which is less direction-dependent than the π-π interaction. Therefore the usual bathochromic shift is observed in the C-band.[1] The increased intensity of absorption is quite marked (cf. Table 1) and can be explained by the evening out of the energy levels of the ground states, which will affect the ratios of the absorption intensities in the C- and B- bands. This is illustrated in Figure 2.

15. Forbes, W.F. and Mueller, W.A. Can. J. Chem. 34:1542. 1956.

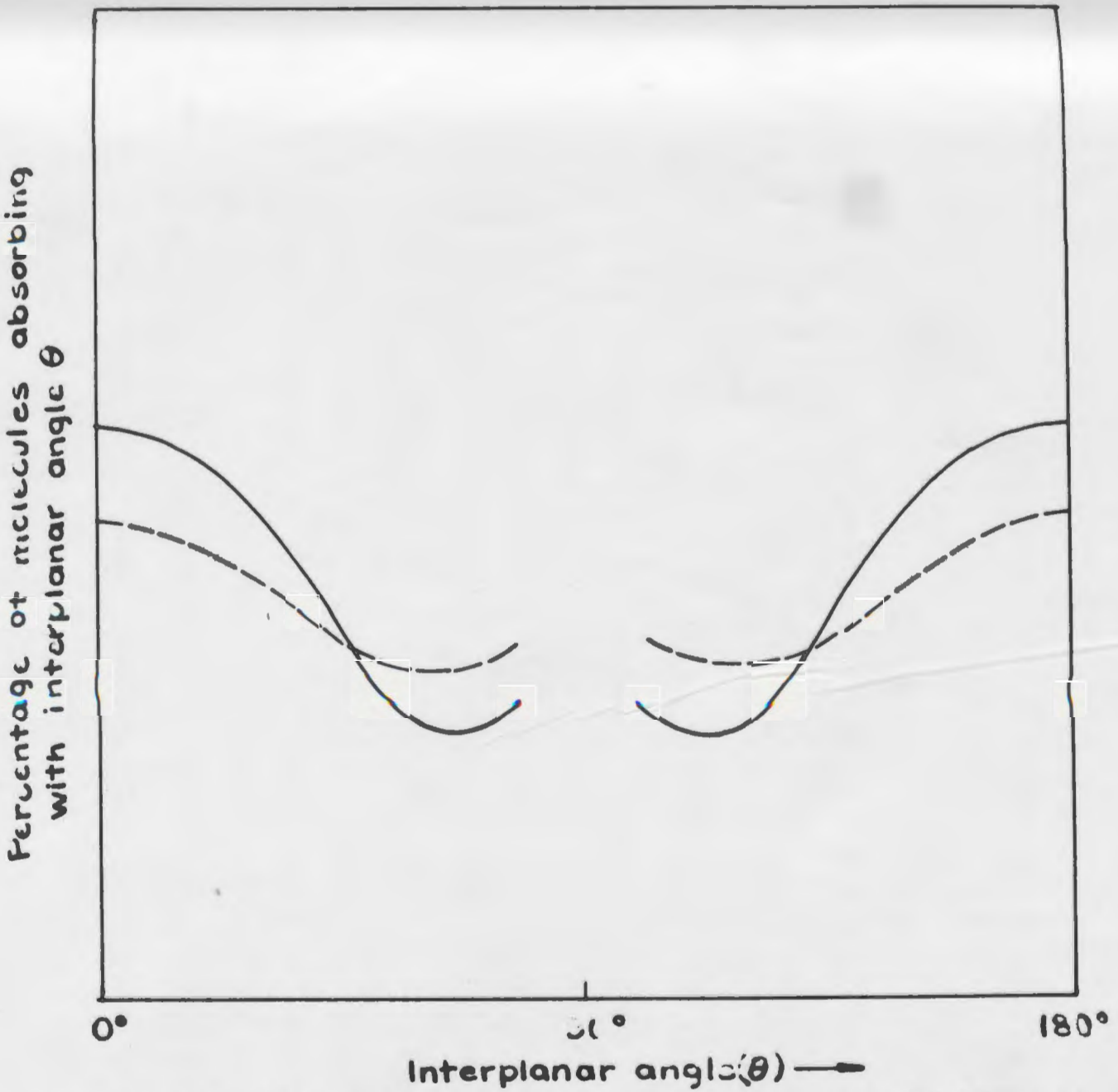


Figure 2. Schematic representation of the distribution curves for benzenoid molecules - in the ground state - contributing to the observed absorption.
Curve 1 (——); in the absence of amino- or similar substituent.
Curve 2 (----); with amino- or similar substituent.

This effect, being characteristic of the C-band, may be used in the assignment of absorption bands. An example of this type of application is provided by the long-wavelength band of ortho-bridged diphenyls (see Table 3 of a discussion about diphenyls[16]) where it may be noted that the introduction of ortho-methoxyl groups considerably increases the intensity of the band; this suggests that the long-wavelength band is a C-band. The reversed effect on B and C-bands of a methoxy-group in the ortho and para-positions has already been noted by Burawoy and co-workers[17], although these authors propose a different explanation for the B- and C-bands.

Generally, the effect of mesomeric interaction may be deduced in a similar manner, namely by considering distribution curves. If thus the operation of the mesomeric effect is confined principally to one plane, a large mesomeric effect will - by maintaining a large percentage of molecules in the near-planar or planar conformation - reduce the percentage of molecules subtending a large interplanar angle. Since a large interplanar angle aids absorption leading to the C-band, a large mesomeric effect will generally give rise to a low intensity C-band and vice versa. This generalisation is well illustrated by a number of compounds. For example, nitrobenzenes on account of the large mesomeric effect of the coplanar nitro group, exhibit only a weak C-band, which is often submerged. Another example is the order of the observed intensities in halogen-substituted benzenes which can also be rationalised from the above generalisation; if the mesomeric

16. Braude, E.A. and Forbes, W.F. J. Chem. Soc. 3776. 1955.
17. Burawoy, A., Cais, M., Chamberlain, J.T., Liversedge, F., and Thompson, A.R. J. Chem. Soc. 3721. 1955.

effect decreases, as in fluorosubstituted benzenes, the intensity of the C-band increases, and thus accounts for the order of the intensities which apparently correspond to the inductive effect.

The difficulty of finding a suitable reference compound for the study of the ortho-effect in the C-band can now be appreciated. For para-disubstituted benzenes there is maximum resonance interaction and hence the C-band is weak. This weak C-band will moreover only make a satisfactory reference spectrum for the study of the ortho-effect if steric inhibition of resonance is negligible, since any change in the resonance energy will now introduce another variable. In the meta-isomers the mesomeric effect is secondary and this accounts for the generally more pronounced C-band. If in the ortho-isomer the steric interaction destroys most of the mesomeric interaction by increasing the angle of twist, the mesomeric effect will again be secondary and thus the meta- and ortho-isomers may resemble each other. However, this agreement between ortho- and meta-isomers is by no means general, because steric inhibition of conjugation in neutral solution is seldom complete, and because other effects such as hydrogen bonding frequently play a part.[18]

The effect of the ortho-substituents is perhaps best estimated by using the absorption of the mono-substituted parent compound and then allowing for both the mesomeric and steric interaction of the second substituent. As in B-bands, the absorption of the C-bands may normally be correlated by considering only mesomeric and steric effects. The

18. Forbes, W.F., Mueller, W.A., Ralph, A.S. and Templeton, J.F. Unpublished information.

bands differ in that for the C-band, the mesomeric effect will weaken and steric effects strengthen this band (by decreasing mesomeric effect and by increasing the mean interplanar angle); for the B-band the mesomeric effect reinforces the band while steric effects weaken it.[1,2,5,19]

It follows from the above sections that differences in intensity ratios will normally be more marked than differences in wavelength ratios, since only intensity changes in the two bands are frequently in opposing directions.

SOLVENT EFFECTS

The effect of substituents has indicated (see above) that the transitions leading to the B-band and C-band are essentially of similar character. Confirmatory evidence should be forthcoming from a study of solvent effects since these have been shown to be characteristic for other bands.[20] With this in mind the B- and C-bands have been determined in different solvents, firstly in ethanol and cyclohexane (see Table 1), then in dioxane-water mixtures[18] and finally in concentrated sulfuric acid (see Table II).

Changing the solvent from ethanol or 95% aqueous ethanol to cyclohexane or ether generally reinforces the C-band, and thus assists in defining the band. For example, in para-halogen substituted benzoic acids it is necessary to determine the spectra in hydrocarbon solvents, before the C-band may be identified (cf. Table I). Otherwise no important changes are apparent between these two types of solvent. Certain

19. Forbes, W.F. and Sheratte, M.B. Can. J. Chem. 33:1829. 1955.
20. Burawoy, A. Discuss. Faraday Soc. 9:70. 1950.

TABLE II

VARIATION OF ABSORPTION SPECTRA WITH ACIDITY

Compound	B-Band				C-Band			
	in Ethanol		in H_2SO_4		in Ethanol		in H_2SO_4	
	λ_{max} mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}
Acetophenone	240	12,500[1]	293	20,000	276	1000[1]	ca.320	1900
2-Methylacetophenone	242	8500[1]	293	14,000	283	1250[1]	354	1600
3-Methylacetophenone	245	11,100	300	20,700	350	2050	285	1300
4-Methylacetophenone	252	15,000[1]			ca. 278	850[1]	ca. 350	2000
Benzaldehyde	242	14,000[2]	293	21,000	280 290	1400[2] 1200	335	2000
2-Methylbenzaldehyde	251	13,000[2]	296	17,000	291	1700[2]	364	2000
4-Methylbenzaldehyde	251	15,000[2]	309	23,000	279	1200[2]	-	-
Benzoic acid	227	11,000[1]	260	15,500	271 279	760[1] 550	294	2000
2-Methylbenzoic acid	228	5000[1]	264	16,000	279	725[1]	312	2700
3-Methylbenzoic acid	332	9000[1]	265	16,400	279	1000	310	2200
4-Methylbenzoic acid	236	14,000[1]	275	21,100				
4-Nitroacetophenone[3]	262	14,000	286	21,500	ca.310	1600	ca. 340	3200
Nitrobenzene	258	8000	287.5	8600	-	-	ca. 302	7200

[1] (Table I); [2](in n-hexane or cyclohexane, 4); [3](21).

minor changes can be more satisfactorily examined by considering dioxane-water mixtures and will therefore be discussed then.

Examination of the B- and C-bands for acetophenones shows that, in agreement with Burawoy et al.,[17] the B- and C-bands generally are displaced to longer wavelength on increasing the dielectric constant of the solvent (cf.[21] and the changes observed in Table I on changing the solvent from cyclohexane to ethanol).

It should be noted however (cf. Experimental, Table I, and[18]), that there are a number of exceptions to this general rule. Thus, for example, values are dependent on the concentration of the solution.[18] Next, values for benzoic acids are anomalous, although fairly uniformly so for both B- and C-bands,[18] and lastly, intensity changes do not always follow the same pattern in the two bands.

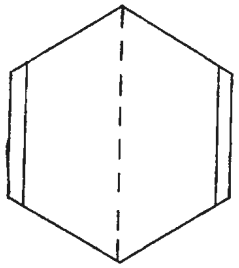
Addition of sulphuric acid in the acetophenone series generally displaces both bands to longer wavelength. The absorption spectra of some B- and C-bands in concentrated sulfuric acid are shown in Table II and[20].

It may be noted that the bathochromic shift due to the ortho-substituent in the C-bands for sulfuric acid spectra again supports the general hypothesis as does the overall similarity of the changes observed in both bands on increasing the proton availability of the solvent (see Table II).

21. Tanaka, J., Nagakura, S., and Kobayashi, M. J. Chem. Physics. 24:311. 1956.

DISCUSSION

The C-band has been characterized as due to transitions involving homopolar structures of type I,[10,11,22,23,24,25] which are "forbidden" transitions. It is usually assumed to correspond to the A_{1g} -- B_{2u} transition in benzene.[21] This assignment is supported by calculation of the expected absorption intensities. However, observed substitution effects[10,23,26] do not completely support this assignment.



I

If, for example, calculations are extended to more complicated molecules[10,27,28] it is found that good agreement between the calculated and observed intensity is only seldom obtained. According to the hypothesis it is unnecessary to invoke the inductive effect in order to account for the C-band of halogen-substituted benzenoid compounds;[1] further the occasional similarity in the frequency and intensity of absorption of ortho- and meta-substituted compounds for the C-band, which has received a quantum mechanical interpretation by Forster[15] is only of limited value in correlating the C-bands in the type of compounds discussed in this thesis. It may be that these calculations are correct for the ground states — and hence might incidentally be expected to hold for the B-band also — but that the

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superimposed effect of the electronic excited states so alters the spectrum that any original ortho-meta similarity is often hidden (in previous sections, and[2,3,5,6,19,29]). A similar comment would apply to the intensity ratios proposed by Sklar.[28]

It has also been supposed[14,30,31,32,33] that acetophenones absorb light along two non-identical axes, which are perpendicular to each other. One optical axis would then correspond to transitions which give rise to the B-band, whereas the other optical axis correlates with the absorption of the C-band. This concept of the directional incidence of light waves on the molecule — which receives support from the absorption of polarized ultraviolet light and indicates that electric vectors (i.e., the direction of motion of the π-electrons) associated with both bands lie in the plane of the ring[8,46] — may readily be correlated with the hypothesis. Since the excited states are direction-dependent, the angle of incidence would be expected to alter the probability of absorption.

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32. Lewis, C. and Calvin, M. Chem. Revs. 25:273. 1939.
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34. Heilbron, Sir I, and Burbury, H.M. Dictionary of Organic Compounds, Eyre and Spottiswodle Ltd., London. 1946.

PREPARATION OF COMPOUNDS

The steric effects, as shown in the spectral properties, are also evident in some of the chemical reactions employed in the preparation of compounds. For example, yields of ortho-derivatives in halogen-substituted acetophenones are small (see Table III). The refractive indices for fluoro- and chloro-acetophenones also indicate an order para > meta > ortho (see Table III). It seems probable that this order is conditioned by steric effects, at least to some extent.

Except for minor deviations in procedure, the compounds, if not commercially available, were prepared by standard methods as described in the literature. Purification was effected by fractional crystallisation, by distillation under vacuum, by vacuum sublimation, or by a combination of these methods, as was appropriate in each case.

EXPERIMENTAL

The physical constants of the compounds are listed in Table III.

2- and 3-Methylacetophenones were prepared by the method previously described.[1] The fluoracetophenones, 2-chloroacetophenones, and 2-bromoacetophenone were prepared from the corresponding acid chlorides by treatment with an excess of dimethyl cadmium (cf.[35]). Purification was effected by distillation in vacuo.

3-Chloro-, 3-bromo-, 3-iodo-, and 3-hydroxy-acetophenone were obtained by diazotisation of 3-aminoacetophenone, followed by the standard Sandmeyer procedure.

TABLE III

PHYSICAL CONSTANTS OF ACETOPHENONES

Acetophenone	Melting Point or Boiling Point and Refractive Index	Yield	Reported Value of Physical Constants
3-Methyl-	b.p. 65-71°, 3 mm., n_D^{22} 1.5170	57%	b.p. 109°, 12 mm., n_D^{15} 1.533 (3)
2-Fluoro-	b.p. 63°, 9 mm., $n_D^{22.5}$ 1.5068	35%	b.p. 80-85°, 16 mm. (37)
3-Fluoro-	b.p. 57°, 3 mm., n_D^{19} 1.5083	65%	b.p. 81°, 9 mm. (38)
4-Fluoro-	b.p. 62°, 4 mm., n_D^{21} 1.5096	47%	b.p. 79°, 10 mm., n_D^{25} 1.5081 (39)
2-Chloro-	b.p. 75°, 4 mm., n_D^{23} 1.5147	30%	b.p. 85-87.5°, 5 mm. (40)
3-Chloro-	b.p. 88°, 4 mm., n_D^{23} 1.5494	80%	b.p. 80°, 2.5 mm., n_D^{20} 1.5494 (41)
4-Chloro-	b.p. 83°, 4 mm., n_D^{20} 1.5558	-	b.p. 103-105°, 11 mm. n_D^{20} 1.5582 (42)
2-Bromo-			b.p. 131-135°, 20 mm. n_D^{20} 1.5667-1.5678 (43)
3-Bromo-			b.p. 131-132°, 17 mm. n_D^{20} 1.5755 (34)
3-Iodo-	$n_D^{23.5}$ 1.6228	40%	b.p. 117°, 4 mm. n_D^{20} 1.6220 (19)

4-Iodo-	m.p. 84°	40%	m.p. 85° (34)
2-Hydroxy-	b.p. 72°, 4 mm. n_D^{21} 1.5590	30%	b.p. 96°, 10 mm., n_D^{21} 1.558 (18)
3-Hydroxy-	m.p. 95-96°	50%	m.p. 96° (18)
4-Hydroxy-	m.p. 104°	26%	m.p. 109° (18)
2-Amino-	b.p. 97°, 4 mm., n_D^{23} 1.6096	63%	b.p. 124°, 10 mm. (18)
3-Amino-	m.p. 95-96°	-	mλ m.p. 98-99° (18)
4-Amino-	m.p. 104-105°	-	m.p. 106° (18)
2-Nitro-	b.p. 119°, 4 mm., $n_D^{21.5}$ 1.5560	-	b.p. 112.5-113.5°, 2 mm. n_D^{25} 1.5530 (44)
3-Nitro-	m.p. 78°	-	m.p. 76-78° (45)
4-Nitro-	m.p. 79°	-	m.p. 78.5-80° (44)

4-Bromo-, and 4-iodo-acetophenones were obtained by Friedel-Crafts acetylation of the halogen-substituted benzenes using acetyl chloride and aluminum chloride. Purification was effected by crystallisation and vacuum sublimation.

2-Hydroxy- and 4-hydroxyacetophenones were prepared by means of a Fries rearrangement of phenyl acetate, using aluminum chloride. The ortho-compound was purified by vacuum distillation, while the para-isomer crystallised from ethanol.

2-Aminoacetophenone was obtained by reduction of 2-nitro-acetophenone with tin and hydrochloric acid.

The remaining acetophenones were purified from the commercially available compounds. 3-Nitro- and 4-nitroacetophenones were vacuum sublimed, and 4-chloroacetophenone was purified by means of semicarbazone.

The preparation of the benzoic acids has previously been described.[19]

Commercially available sulphuric acid was used in the determination of the acid spectra.

For description of instrument used and method of purification of dioxane see experimental Part II of this thesis.

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38. Evans, D.P., Morgan, V.G. and Watson, H.B. J. Chem. Soc. 1172. 1935.
39. Renoll, M.W. J. Am. Chem. Soc. 68: 1159. 1946.
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41. Leonard, N.J. and Boyd, S.N. Jr. J. Org. Chem. 11: 405. 1946.
42. Matsui, E. J. Chem. Soc. Ind. Japan 45: 412. 1942.
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45. Blatt, A.H. Organic Syntheses, Coll. Vol. 2, John Wiley and Sons, Inc., New York. 1950.
46. Craig, D.P. and Lyons, L. E. Nature, 169:1102. 1952.

ABSTRACT

Hydrogen bonding, which is known to give rise to dimer formation in benzoic acids and similar compounds, may affect solution spectra by intermolecular and/or by intramolecular bond formation. Generally environmental factors affecting absorption spectra can be divided into three types:- Intermolecular hydrogen bonding between solute molecules only; intermolecular hydrogen bonding between solute and solvent molecules; and orientation effects involving the formation of hydrogen bonds.

Evidence for the occurrence of these types of interaction is deduced from ultraviolet spectra and various implications and applications of the spectral analysis are discussed.

PART II. THE STUDY OF HYDROGEN BONDING AND SIMILAR EFFECTS BY MEANS OF ULTRAVIOLET ABSORPTION.

INTRODUCTION

Hydrogen bonding has previously been mentioned as a possible cause of certain anomalous spectra.[1,2,3,4] Hydrogen bonding may be intermolecular or intramolecular, already intramolecular hydrogen bonding has been used to explain the ultraviolet spectra of o-hydroxyacetophenone and salicylic acid.[5,6] Intermolecular hydrogen bonding would be expected to occur firstly because dimer formation in benzoic acids is a well-known phenomenon in infrared spectroscopy[7,8,9] and secondly because certain changes in ultraviolet absorption spectra on changing the solvent have been ascribed to intermolecular hydrogen bonding.[10,11,12,13,14,15] Also the dependence of ultraviolet absorption spectra on the solution concentration has been noted by several workers.[16,17,18,19,20]

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2. Forbes, W.F. and Mueller, W.A., Can. J. Chem. 34:1542. 1956.
3. Forbes, W.F. and Mueller, W.A., Can. J. Chem. 35 (in press)
4. Part I. This Thesis.
5. Dannenberg, H., Z Naturforschg. 46:327. 1949.
6. Cram, D.J. and Cranz, F.W., J. Am. Chem. Soc. 72:595. 1950.
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8. Davies, M., and Griffiths, D.M.L., J. Chem. Soc. 132. 1955.
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15. Nagakura, S. and Baba, H., J. Am. Chem. Soc. 74:5693. 1952.

Intermolecular hydrogen bonding, for which there is therefore some evidence, may now be divided into two types. Firstly, intermolecular hydrogen bonding occurring between solute molecules only and secondly, intermolecular hydrogen bonding occurring between solvent and solute molecules.

Intermolecular hydrogen bonding between solute molecules only, should be a function of the concentration, and consequently should be susceptible to independent investigation, particularly since examples can be taken which largely eliminate intramolecular hydrogen bonding and steric effects. Monosubstituted benzenes, and benzoic acids provide a satisfactory starting point, particularly since the latter has previously been investigated.[21] In this investigation it was found that, although dimer formation was anticipated, the B-bands could be satisfactorily correlated without considering the effect of hydrogen bonding. This thesis may be considered as an extension of this previous study.

The effect of intermolecular hydrogen bonding between solvent and solute molecules and/or orientation effects may be investigated by choosing examples, in which steric effects and intramolecular hydrogen bonding have been kept small, and which further do not show the concentration changes as ascribed to solute-

16. Keussler, V. v., Z. Elektrochem. 58:136. 1956.
17. Hirschberg, Y., Knott, E.B. and Fisher, E., J. Chem. Soc. 3313. 1955.
18. Beinert, H., J. Am. Chem. Soc. 78:5323. 1956.
19. Koizumi, M. and Mataga, N., Bull. Chem. Soc. Japan 27:194. 1954. cf. Chem. Abs. 49:7382. 1955.
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21. Forbes, W.F. and Sheratte, M.B., Can. J. Chem. 33:1829. 1955.

solute hydrogen bonding. Such examples are available and these will be examined in a later section.

THE DEPENDENCE OF ULTRAVIOLET ABSORPTION SPECTRA ON CONCENTRATION (INTERMOLECULAR HYDROGEN BONDING BETWEEN SOLUTE MOLECULES ONLY)

In ethanolic solution, it has been found that benzoic acid gives rise to a definite increase in the observed absorption intensity on increasing the concentration. This series of data along with about 25 other series are listed in Table I, and almost all of these show distinct increases of absorption intensity (ε) with increased solution concentration.

It appears that the increase is not confined to the carbonyl group, since a considerable increase is obtained for methyl benzoate; nor does it seem necessarily limited to the oxygen atom since a change--although much smaller--is also obtained for diphenyl (see Tables I and II). The only listed exception is the spectrum of salicylic acid in dioxane, where the opposite change is observed. This exception may be due to interfering effects, such as intramolecular hydrogen bonding, which would be expected to be important in compound like salicylic acid (cf. also the absence of the usual changes ascribed to association for o-chlorophenol[22] and for catechol[23], for ortho-substituted amines[24] and for ortho-substituted cyclohexylphenols.[14]

22. Nagakura, S., J. Chem. Soc. Japan, Pure Chem. Sect. 75:734. 1954. cf. Chem. Abs. 48:10,434. 1954.
23. Joule, L., Carpeni, G. and Hamann, Y. Bull. Soc. Chim., France. 448. 1956. cf. Chem. Abs. 50:11,819. 1956.
24. Gordy, W. and Stangord, S.C., J. Am. Chem. Soc. 62:497. 1940.

For a number of other compounds, such as acetophenone which will be listed and discussed later, there is no evidence for concentration dependence; this may be taken to indicate that for these molecules no hydrogen bonding between solute molecules occurs.

With one exception, therefore, the data in Table I are all consistent with the initial assumption that the observed changes are related to intermolecular hydrogen bonding. The hypothesis is also supported by the much greater solubility of phenol and aniline compared to nitrobenzene and benzene in water[25]; by the reported absence of association in acetophenone as judged from infrared and Raman studies[26], from other infrared studies,[27] and particularly from temperature changes on spectra, where it has been shown for phenol and other compounds that increasing the temperature has the same effect as reducing the concentration of the solute, that is a decreased absorption intensity without wavelength change.[14,28]

Several points which will be examined again later, may next be mentioned. Thus firstly, since association apparently occurs even between hydrocarbon molecules (e.g. diphenyl in cyclohexane; see Table I), the choice of solvent is important. A solvent like ethanol or water, because of the high dielectric constant, may be expected to associate more readily with a solute molecule and

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27. Nevilly, M. Compt. rend. 238: 781. 1954. cf. Chem. Abs. 48:8038. 1954.
28. Jones, R.N., Forbes, W.F. and Mueller, W.A. (Unpublished information).

TABLE I

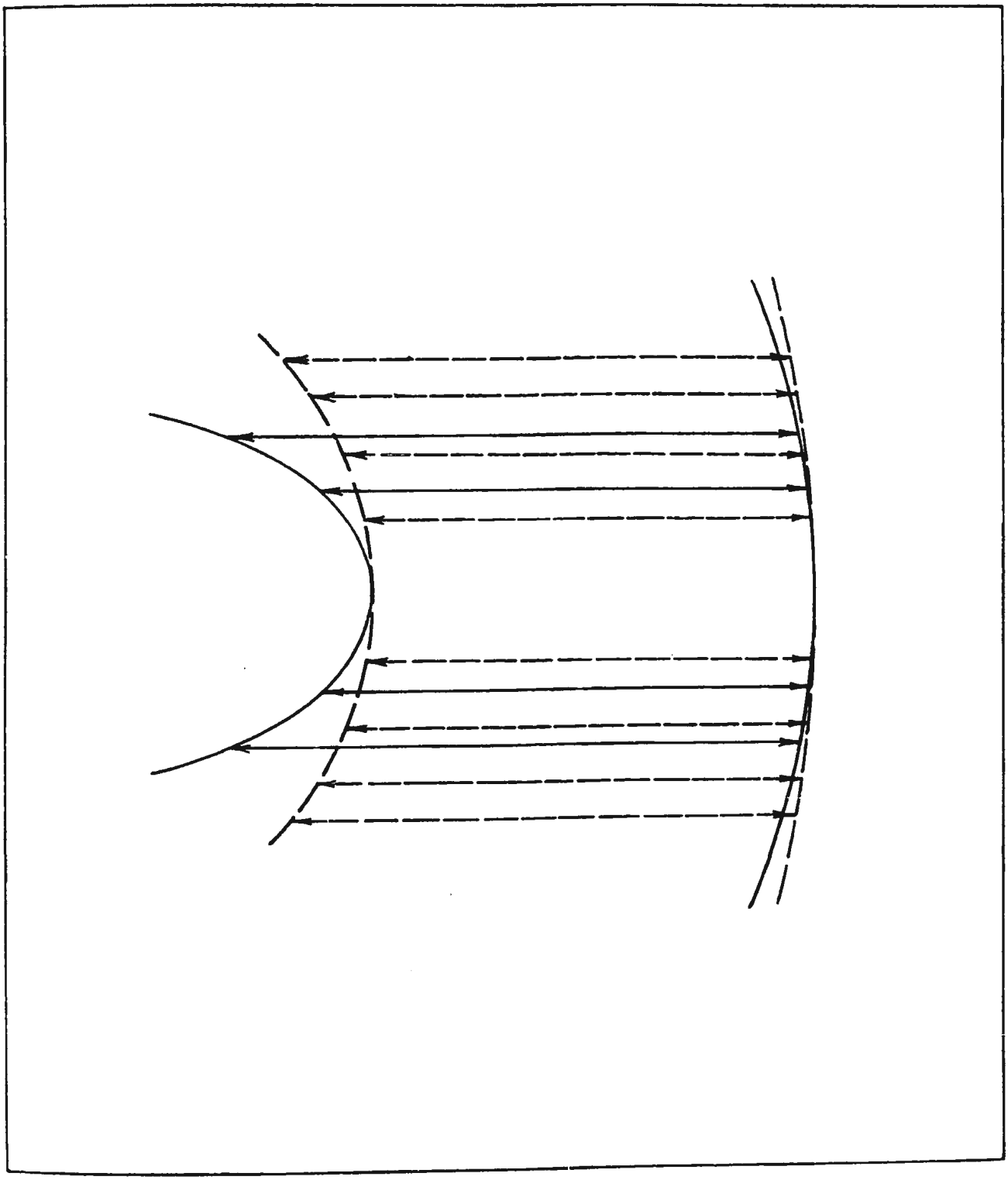
ABSORPTION MAXIMA (B-BANDS) OF COMPOUNDS IN SOLUTIONS OF VARYING CONCENTRATION

(Concentration, c = 2.8×10^{-6} to 6.3×10^{-5} moles/liter; cell lengths are given in brackets)

COMPOUND	SOLVENT	40c(1 mm.) λ_{max}, mμ	40c(1 mm.) ε_{max}	8c(5 mm.) λ_{max} mμ	8c(5 mm.) ε_{max}	4c(10 mm.) λ_{max}, mμ	4c(10 mm.) ε_{max}	2c(20 mm.) λ_{max} mμ	2c(20 mm.) ε_{max}	c(40 mm.) λ_{max} mμ	c(40 mm.) ε_{max}
Benzoic acid	Ethanol	227	11,000	227	10,400						
Methyl benzoate	Ethanol	227	11,800	228	11,300	227-8	10,900	228	9300	228-9	8400
Nitrobenzene	Ethanol	257	8100	257-8	8100	257	8000	258	7800	257-8	7700
3-Aminobenzoic acid	Ethanol	ca. 241	7600	ca. 241	7400	ca. 241	7000			ca. 241	6600
4-Aminobenzoic acid	Ethanol	288	19,200			288	19,000			288	18,200
2-Aminobenzoic acid	Ethanol	247	6900			247	6700			247	6400
Aniline	Cyclohexane	233	9000			233-4	9000	234	9000	234	8000
Diphenyl	Cyclohexane	247	16,200	246	16,300	247	15,900			246	15,600
Benzoic acid	Cyclohexane	232	13,300	231	12,100	230	10,300			229	10,300
3-Fluorobenzoic acid	Cyclohexane	230-1	11,800							227	9700
Benzoic acid	Dioxane	229	11,500	228	11,100	228	11,000	228	9800	228	6200
Benzoic acid	75% aqueous Dioxane	228	11,200	228	10,500	228	11,300	229	10,400	228	10,600
Benzoic acid	50% aqueous Dioxane	228	10,800	228	10,300	228	9800	228	9300	227	9200
Benzoic acid	25% aqueous Dioxane	229	11,500	229	11,000	229	10,800	229	10,700	228	10,700
[illegible] acid	Water	228	11,400	226	9800	225	9500	224	9400	223	9900

3-Fluorobenzoic acid	Cyclohexane	230-1	11,800								
Benzoic acid	Dioxane	229	11,500	228	11,100	228	11,000	228	9800	228	6200
Benzoic acid	75% aqueous Dioxane	228	11,200	228	10,500	228	11,300	229	10,400	228	10,600
Benzoic acid	50% aqueous Dioxane	228	10,800	228	10,300	228	9800	228	9300	227	9200
Benzoic acid	25% aqueous Dioxane	229	11,500	229	11,000	229	10,800	229	10,700	228	10,700
Benzoic acid	Water	228	11,400	226	9800	225	9500	224	9400	223	9900
4-Hydroxybenzoic acid	Dioxane	251	12,500	251	12,300	251	13,000	251	12,000	251	9200
4-Hydroxybenzoic acid	50% aqueous Dioxane	255	14,300	254	13,800	252	13,800	251	10,000	250	10,000
4-Hydroxybenzoic acid	25% aqueous Dioxane	251-2	13,600	251	12,500	249	13,000	246-7	12,000	245	12,700
4-Hydroxybenzoic acid	Water	251	12,100	249	11,200	247	11,600	246	11,300	245	12,000
Salicylic acid	Dioxane	237	9500	237	9500	237	9500	237	9500	237	9500
Salicylic acid	75% aqueous Dioxane	236	7500			236	7700	236	5700	235-6	5200
Salicylic acid	50% aqueous Dioxane	235	6800	234	6600	232	6100	231	5300	228-9	5100
Salicylic acid	25% aqueous Dioxane	233	7000	231	6400	230	6400	230	6000	229	6400
Salicylic acid	Water	231-2	7000	231	6900	230	6800	230	6900	230	6800
Benzaldehyde[1]	Dioxane	248	12,200	248		248	10,800	248	10,300	248	8000
Benzaldehyde	50% aqueous Dioxane	247	12,400			247	11,600	247	11,700	247	10,500
Benzaldehyde	Water	243	12,600			243	12,400			243	11,800
2-Aminoacetophenone	Dioxane	253-4	5700	254	5600	254	5000	254	4700	255	3100
2-Aminoacetophenone	75% aqueous Dioxane	254-5	5900	255	5800	255	5600	255	5100	255	4800
Nitrobenzene	Dioxane	257-8	8400	258	8200	258	8100	258	8000	259	7400

[1](40).



ure 1. Schematic representation of potential energy curves and electronic nsitions for benzoic acid in the monomeric form (full lines) compared to enzoic acid in the dimeric form (dashed lines).

may consequently reduce the association between solute molecules. This follows because in a solvent of high dielectric constant, other forces will compete with the association between solute molecules. This is confirmed by the observed changes in absorption intensity for benzoic acid which are seen from Table I to be more pronounced in inert solvents than in ethanol. Consequently, a solvent such as dioxane or cyclohexane will generally be preferred in studying this type of hydrogen bonding.[16] In the present study both dioxane and cyclohexane were frequently used; the latter because of its very inactive nature, the former because of its ability to form mixtures with water over a wide range of dielectric constants.

Spectra in dioxane are also of interest because it is believed on the basis of freezing point measurements,[29] and infrared data[30] that benzoic acids are monomeric in dioxane. This belief is not supported from the ultraviolet spectral data (see Table I) and therefore suggests that intensity measurements in the ultraviolet may be a more sensitive index of intermolecular association.

It may be next noted that the observed intensity changes in Table I are not normally accompanied by any appreciable wavelength change and with this additional point in mind the possible factors causing the observed changes may now be examined.

One of the interpretations suggesting itself for the observed change is that association, by withdrawing electrons from the electronic cloud in the carboxyl group, increases the planarity

29. Lassetre, Chem. Revs. 20:277. 1937.
30. Flett, M. St. C. J. Chem. Soc. 962. 1951.

of the molecule. The resulting decreased steric interaction can account for the increased absorption intensity, but would be expected to give rise to a bathochromic shift[1,31] which does not occur for the examples listed in Table I.

An alternative interpretation is that association decreases the force constant of twist about the bond linking the carboxyl group to the benzene ring. This is illustrated in Fig. 1.

The decreased force constant somewhat flattens the potential energy curves of the ground and excited states and this increases the absorption intensity, whereas the wavelength of absorption remains approximately constant. Inspection of Table I shows that this interpretation accounts for most of the observed changes and may consequently provisionally be accepted as the predominant factor causing the observed changes.

A third interpretation is to suppose that increased association (involving non-bonded electrons of the carboxyl group) increases the energy of excitation, because of the greater amount of energy required to excite partially bound electrons. Since this greater energy would cause a hypsochromic shift it is clearly not the predominant factor for the compounds studied (see Table I; it should be noted, however, that this interpretation can be used to explain the association of organic molecules with water molecules).

The hypothesis that association, chiefly by varying the force constant, causes the observed changes also receives support from a number of other independent observations. Thus firstly, a smaller force constant - assuming the hypothesis proposed

31. Forbes, W.F. and Mueller, W.A., Can. J. Chem. 34:1347. 1956.

for the C-band[4] - would frequently produce similar changes in both B- and C-bands. This similarity is in fact observed (see Tables I and II) and incidentally disfavours the first interpretation (see above), since increased planarity would generally cause a C-band of decreased intensity.[4]

Next, an altered force constant would be expected to be obtainable also on introducing substituents in a molecule, and this supposition is found to be true. For example, m-terphyenyl ($\lambda_{max.}$ 252 mμ, ε = 44,000) absorbs at approximately the same wavelength as diphenyl ($\lambda_{max.}$ 252 mμ, ε = 18,000), but rather surprisingly with more than twice the absorption intensity of diphenyl.[32] This suggests that possibly an analogous effect to the above mentioned association occurs; namely that the third phenyl ring weakens the force constant for the central bonds and in this way causes the characteristic absorption intensity increment without appreciable wavelength shift.

A similar effect may account for the previously noted but unexplained similarity between the spectra of nitrobenzoic acids and nitrobenzene.[21] The negative mesomeric effect of both substituents in nitrobenzoic acids can be supposed to de-activate the benzene nucleus and this explains the absence of any apparent interaction between the two substituents in para- and meta-nitrobenzoic acids as indicated by the lack of any appreciable wavelength shift. However, according to the hypothesis, a secondary effect will operate which in the para-isomer will tend to reduce the force constant of the bond linking the nitro group to the benzene ring

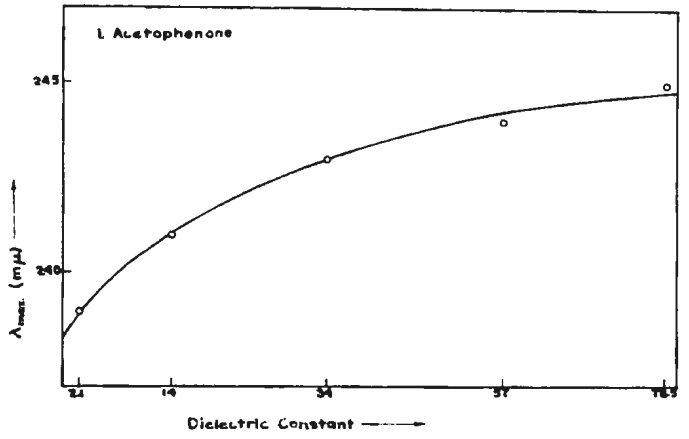
32. Gillam, A.E. and Hey, D.H., J. Chem. Soc. 1170, 1939.

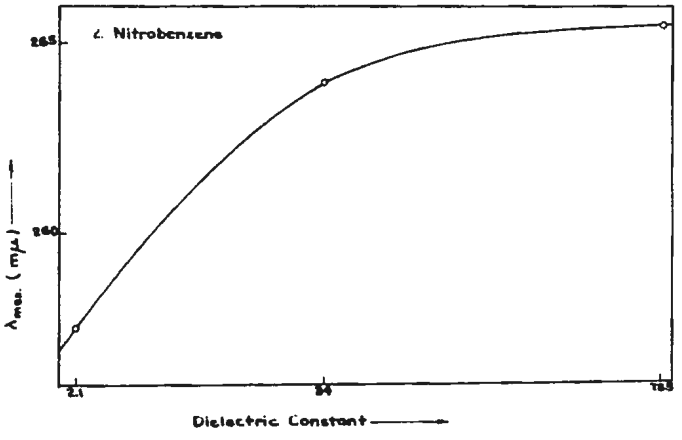
TABLE II

ABSORPTION MAXIMA (C-BANDS) OF COMPOUNDS IN SOLUTIONS OF VARYING CONCENTRATION

(Concentration, c = 2.8×10^{-6} to 6.3×10^{-5} moles/liter; cell lengths are given in brackets)

COMPOUND	SOLVENT	40c(1 mm.)		8c(2 mm.)		4c (10 mm.)		2c(20 mm.)		c(40 mm.)	
		λ_{max} mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max} mμ	ε_{max}.	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}
4-Hydroxybenzoic acid	50% aqueous Dioxane			271	7100	271	6900	271	6600	271	6200
4-Hydroxybenzoic acid	25% aqueous Dioxane	271	7300	271	6900			271	5300	271	4900
4-Hydroxybenzoic acid	Water			270	5900	270	5400	270	4200	270	3600
Salicylic acid	50% aqueous Dioxane	301	3600	300	3500	300	3500	298	3500	296	3400
Aniline	Cyclohexane	286	1930	286	1830	286	1830	286	1760	286	1660
Phenol	Cyclohexane	263	1500	263	1400	263	1400	263	1300	263	1100
		269	2200	269	2100	269	2100	269	2000	269	1900
		276	2100	276	2000	276	2000	276	1900	276	1700





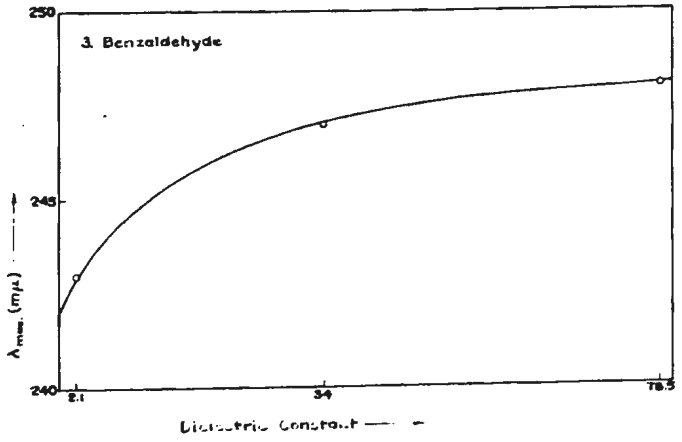


Figure 2. The dependence of maximal wavelength on the dielectric constant of the solvent.

and thus cause the increased absorption intensity (λmax 258 mμ, ε = 11,000). Since this represents an interaction of para substituents on each other, the interaction can be regarded as mesomeric[3], and consequently it would be expected to operate preferentially in the para-isomer than in the meta-isomer. This is borne out by the data since the meta-isomer absorbs with approximately the same intensity (λmax 255 mμ, ε = 8500) as nitrobenzene (λmax 258 mμ, ε = 8500). In the ortho-isomer, steric interference inhibits the conjugation between the nitro-group and the benzene ring and only an inflection appears at approximately 255 mμ, ε = 3500.

This type of explanation may also be used to explain more fundamentally the increased absorption intensity of phenyl benzoate (λmax 230 mμ, ε = 15,000) compared to benzoic acid (λmax 227 mμ, ε = 11,000[21]); and other "anomalous" intensity changes.[33]

THE EFFECT OF DIELECTRIC CONSTANT

In the previous section it was shown that definite changes, which may be ascribed to association, are observed for benzoic acids and other compounds. On increasing the concentration of these compounds an increased absorption intensity is observed, accompanied occasionally by a smaller wavelength shift. The intensity change is large for benzoic acid and much smaller for nitrobenzene (in dioxane) and diphenyl (in cyclohexane).

For compounds like acetophenone in dioxane-water mixture no definite concentration dependence was apparent, and this therefore suggests that acetophenone does not associate under these conditions. This and

33. Forbes, W.F. and Ralph, A.S. Unpublished Information.

some other similar examples are listed in Table III.

The compounds listed in Table III, however, on changing the dielectric constant of the solvent give rise to another type of change, namely a distinct wavelength shift. This wavelength shift may be assumed to be due to two possible effects, (1) orientation forces acting on the molecule (which itself may be in an associated form), or (2) intermolecular hydrogen bonding, of the type discussed in the previous section, acting between solvent and solute molecules. Both types of interaction would be expected to be influenced by steric interaction.

A typical example which may first be discussed is acetophenone, since it is probable that in this compound the observed changes are caused predominantly by orientation forces for the following reasons:

(1) The spectrum of acetophenone is independent of the concentration over a wide range in different solvents (see Table III), and since, therefore, there is no positive evidence for intermolecular hydrogen bonding as there is for other solute molecules, it seems likely that any appreciable intermolecular hydrogen bonding occurs between solute and solvent molecules.

(2) Hydrogen bonding between solute molecules affects mainly ε values, but a change of dielectric constant of the solvent for acetophenone solutions affects mainly the wavelength of maximal absorption. This again suggests that the two phenomena are not closely related.

(3) An orientation effect would be expected to be greater for nitrobenzene than for acetophenone since the dipole moment for nitrobenzene is larger than that of acetophenone; this is in fact observed.

(4) Infra-red data[26] for acetophenone in various solutions failed to show

TABLE III

ABSORPTION MAXIMA OF COMPOUNDS IN SOLUTIONS OF VARYING DIELECTRIC CONSTANT

COMPOUND	SOLVENT	CONCENTRATION RANGE	λ_{max}, mμ	ϵ_{max}
Acetophenone	Dioxane	4×10^{-4} to 1×10^{-5}	239±1	12,000±1000
Acetophenone	75% aqueous Dioxane	4×10^{-4} to 1×10^{-5}	241±1	12,800±800
Acetophenone	50% aqueous Dioxane	4×10^{-4} to 1×10^{-5}	243±1	12,000±500
Acetophenone	25% aqueous Dioxane	4×10^{-4} to 1×10^{-5}	244±1	11,500±500
Acetophenone	Water	4×10^{-4} to 1×10^{-5}	244.5±1	12,000±500
Nitrobenzene	Dioxane	8×10^{-4} to 2×10^{-5}	258±1	7800±400
Nitrobenzene	50% aqueous Dioxane	6×10^{-4} to 1.5×10^{-5}	264±1	7800±400
Nitrobenzene	Water	8×10^{-4} to 2×10^{-5}	266±1	7900±400
Benzoic acid	Dioxane	4×10^{-4} to 1×10^{-5}	228±1	
Benzoic acid	75% aqueous Dioxane	4×10^{-4} to 1×10^{-5}	228±1	10,800±500
Benzoic acid	50% aqueous Dioxane	4×10^{-4} to 1×10^{-5}	228±1	9700±500
Benzoic acid	25% aqueous Dioxane	4×10^{-4} to 1×10^{-5}	228±1	10,800±500
Benzoic acid	Water	4×10^{-4} to 1×10^{-5}	224±1	9500±500
Acetophenone (C-Band)	Dioxane	4×10^{-3} to 1×10^{-5}	277±1	1000±50
Acetophenone (C-Band)	75% aqueous Dioxane	4×10^{-3} to 1×10^{-4}	277±1	1100±50
Acetophenone (C-Band)	50% aqueous Dioxane	4×10^{-3} to 1×10^{-4}	278±1	1150±50
Acetophenone (C-Band)	25% aqueous Dioxane	4×10^{-3} to 1×10^{-4}	278±1	1250±50
Acetophenone (C-Band)	Water	4×10^{-3} to 1×10^{-4}	277±1	1300±50

any band doubling, such as would be expected if more than one molecular species were present in solution.

(5) Acetophenone in cyclohexane (λ_{max} 238 mμ, ε = 12,400[4]) in heptane (λ_{max} 238 mμ, ε = 12,600[34]), and in ether (λ_{max} 239 mμ, ε = 12,600[5]) all absorb at very similar wavelength to the value for acetophenone in dioxane (λ_{max} 239 mμ, ε = 12,000 - Table III). All these solvents have in common a low dielectric constant, whereas the absorption of their association products with acetophenone would be expected to be different.

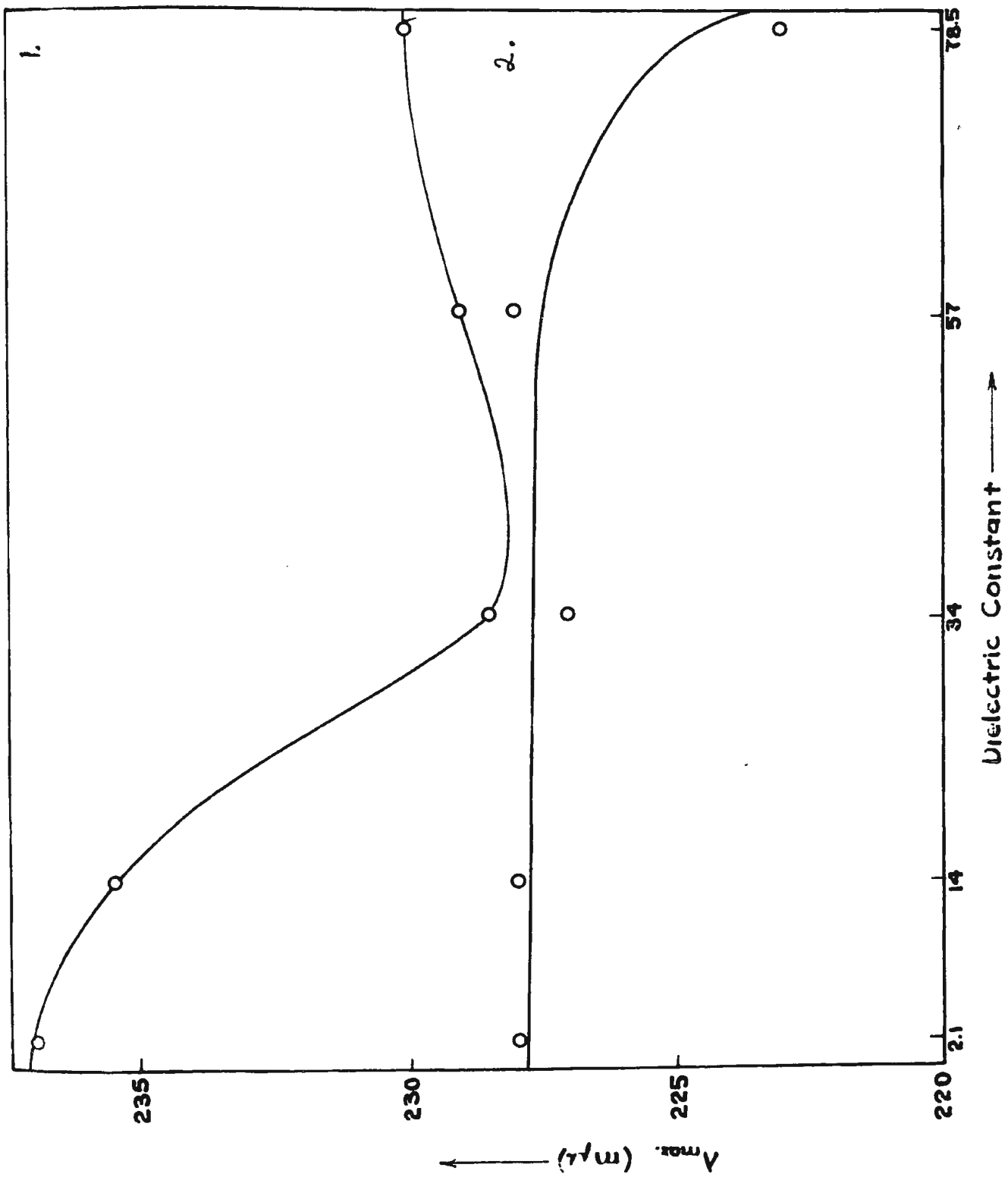
(6) Wavelength changes for the B-band of acetophenone or nitrobenzene are caused by a change in dielectric constant (see Table III). Although the changes are probably not directly proportional to each other, the points apparently lie on a smooth curve (see Fig. 2).

This is not the result to be expected for equilibra between acetophenone - water association products and acetophenone - dioxane association products; there a definite break in the curve would be expected corresponding to the two different molecular species (see Table III and Fig. 3).

(7) Orientation forces would tend to increase the coplanarity of the molecule, steric factors would be expected to be of importance and this has in fact been noted for ortho-substituted phenols[14] where it was shown that in hindered phenols the wavelength change obtained on altering the dielectric constant of the solvent is smaller than usual.

(8) A temperature increase would be expected to have the effect of decreasing the overall double bond character of the central bond and increasing the double bond character of the C - O band. This in turn would lead to an

34. Tanaka, J., Nagakura, S. and Kobayashi, M. J. Chem. Phys. 24:311. 1956.



...re 3. The dependence of maximal wavelength on the dielectric constant of the ...ent for (1) salicylic acid in dilute solution (2) benzoic acid in dilute solution.

increased percentage of non-planar forms and consequently to a changed absorption intensity in the ultraviolet; it would also lead to an increased carbonyl stretched frequency in the vapour phase. The latter prediction is in fact observed[26] and there is also some evidence for the former[28]. It is particularly noteworthy that the wavelength changes observed on changing the dielectric constant of the solvent are not apparently affected on raising the temperature,[14] as would have been expected if mainly intermolecular hydrogen bonding were to account for the wavelength changes.

A physical interpretation for the wavelength changes due to changes in the dielectric constant can now be attempted in terms of the previously suggested hypothesis of increased planarity. This hypothesis was found to be unsatisfactory in accounting for the changes ascribed to association, because a change in wavelength would be expected. However, for the changes described in this section, this required wavelength change is observed and the interpretation does serve to relate the data. In this way, an increased dielectric constant because of dipole-dipole interaction increases the percentage of dipolar forms. This has the effect both of increasing the force constant about the central bond and of causing a bathochromic shift, because dipolar forms lower the energy level of the electronic ground state and even more so the energy level of the electronic excited state.[35] Therefore a bathochromic shift will be observed while intensity changes may either be positive or negative depending on whether the increased force constant or the lowering of the potential energy level is the predominating influence on the absorption probability.

35. Forbes, W.F. and Mueller, W.A. Can. Chem. 33:1145. 1955.

A few additional observations may also be presented at this point. First, the wavelength of maximal absorption of the C-band of acetophenone is apparently independent of the concentration over the range shown in Table III and is also unaffected by changing the dielectric constant of the solvent. Intensity changes of the C-band, on the other hand, rather surprisingly, are apparently proportional to changes in the dielectric constant, that is an increased dielectric constant causes an approximately proportional increase in the molar absorption intensity (ε) (see Table III). However, the scarcity of available data seriously restricts the scope of allowable generalisations at this stage concerning the effect of dielectric constant on the C-band.

Next, whereas the changes with concentration and dielectric constant in the spectra of acetophenone, and probably also of nitrobenzene, can be related using only the hypothesis of orientation forces, a similar simple relation does not hold for other molecules. Thus, for example, the graphs plotting dependence of maximal wavelength against the dielectric constant for benzoic and salicylic acid in dilute solution (see Fig. 3).

This latter observation is also confirmed by the opposite wavelength changes obtained on increasing the dielectric constant for dilute solutions of benzoic acids and p-hydroxybenzoic acids (see Table III) and for solutions of non-aromatic ketones.[36]

36. Mariella, R.P., Raube, R.R. Budde, J. and Moore, C.E. J. Org. Chem. 19:678. 1954.

THE EFFECT OF INTERMOLECULAR HYDROGEN BONDING BETWEEN SOLUTE AND SOLVENT MOLECULES AND OTHER FACTORS ON ULTRAVIOLET ABSORPTION SPECTRA

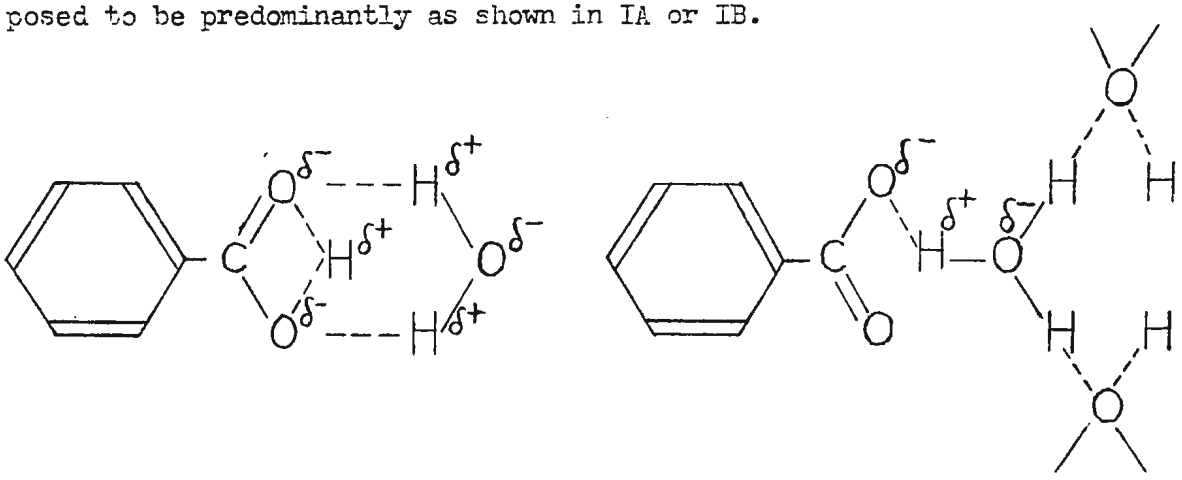
Upon examining some of the exceptional examples mentioned in the above section it is indicated that factors other than those discussed there also affect the ultraviolet spectra. Further the two effects described in the previous sections will frequently interact with one another. At this point some of the more complicated spectra will be described briefly and a tentative proposal for their more complete elucidation will be made.

For example, the spectra of benzoic acid (see Table I, III, and Fig. 3) are consistent with the explanation that (a) dimer formation occurs in more concentrated solution and that (b) in dilute solution intermolecular hydrogen bonding occurs between benzoic acid and solvent molecules. This follows because the dimer is not apparently affected by a change in dielectric constant, and secondly because the changes observed in dilute solution suggest the occurrence of two distinct molecular species. The exact nature of the molecular species involved is, however, still in doubt. It may either represent merely an increased percentage of the anionic species rather than a definite hydrogen bond, as indicated by the absorption of benzoic acid in basic solution at 223 mμ[33] and by some of the previously cited evidence against hydrogen bonding. Alternatively, there is evidence that molecules form external hydrogen bonds with suitable solvents, for example.[11,15,37,38]

37. Klemperer, M., Cronyn, M.W., Maki, A.H., and Pimentel, G.C. J. Am. Chem. Soc. 76: 5846. 1954.
38. Brealey, G.J. and Kasha, M.J. Am. Chem. Soc. 77: 4462. 1955.

This, incidentally would not be unexpected, since benzoic acid for example associates with itself, and there would consequently be reason to suppose that it should similarly associate with suitable solvent molecules.

Fortunately, the above mentioned two suggestions are not mutually exclusive. Again using benzoic acid as an example, the molecular entity present in dilute aqueous solution may be supposed to be predominantly as shown in IA or IB.



IA IB

This type of association would affect the percentage of anionic and neutral molecules present, and this can explain the maximal absorption approaching that of the benzoic acid anion as well as the absence of any wavelength changes in concentrated solution (because of dimer formation). Further, this explanation may represent an example of what is probably quite a general effect, namely that the ordinary polarization effect of solvent molecules is obscured by dipole-dipole and dipole-polarization forces whenever the solute is polar.

The effect of intramolecular hydrogen bonding may also be discerned in some of the spectra. Strong intramolecular hydrogen bonds are known to cause wavelength changes in the ultraviolet of the order of 10-20 mμ[5], and this, not unexpectedly, apparently also affects the usual association between solute molecules (see Table I for the spectrum of salicylic acid, in dioxane, which suggests that salicylic acid in dioxane solution exists to a large extent in the unassociated form). Lastly on changing the dielectric constant of the solvent irregular changes are generally observed for salicylic acid, o-aminoacetophenone and aniline in both B- and C-bands and this again suggests the interaction of a number of different effects. The relevant spectra are recorded in Table IV.

EXPERIMENTAL

The ultraviolet absorption spectra were determined by standard methods using a Unicam SP 500 spectrophotometer. Concentrations were adjusted mainly by using quartz cells of suitable path length, except for aniline, where the concentration varied from 6.7×10^{-3} moles/liter for the 1mm. cell to 1.3×10^{-3} moles/liter for the 40 mm. cell. The concentration was also adjusted so that the optical density readings were in the 0.4-0.5 region whenever possible. For many of the compounds in each solvent at least two independent sets of observations were made, although if the trend of the change was established only a single determination was made.

The compounds were purified by standard methods as described in the literature. Dioxane was purified by the method of Hess and Frahm[39] which consisted in refluxing the crude dioxane with hydrochloric dilute acid under nitrogen for 12 hours, and removal of the hydrochloric acid and water by treatment with potassium hydroxide and then refluxing the dioxane with sodium for 10 hours. The distilled material was stored under nitrogen. Generally purification was considered adequate when additional processing resulted in no further measurable changes in the intensity of absorption. Aqueous dioxane solvent mixtures (volume percentages) were made up volumetrically. All solutions were stored under nitrogen.

The maximal wavelength and corresponding absorption intensities are recorded in Tables I, II, III, and IV.

39. Hess and Frahm, Ber., 71: 2627. 1938.
40. Dearden, J.C. and Forbes, W.F. Unpublished information.

TABLE IV

ABSORPTION MAXIMA OF SALICYLIC ACID o-AMINOACETOPHENONE AND ANILINE IN SOLUTIONS OF VARYING DIELECTRIC CONSTANT

(Concentration, c = 6.4×10^{-4} to 1.6×10^{-5} moles/liter; except for aniline cell lengths are given in brackets)

COMPOUND	SOLVENT	40c(1mm.)		8c(5mm.)		4c(10mm.)		2c(20mm.)		c(40 mm.)	
		λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}	λ_{max}, mμ	ε_{max}
Salicylic acid (B-Band)	Dioxane	237	8400	236-7	8600	237	9400	237	10,400	237	9900
	75% aqueous Dioxane	236	7500			236	7700	236	5700	235-6	5200
	50% aqueous Dioxane	235	6800	234	6600	232	6100	231	5300	228-9	5100
	25% aqueous Dioxane	233	7000	231	6400	230	6400	230	6000	229	6400
	Water	231-2	7000	231	6900	230	6800	230	6900	230	6800
Salicylic acid (C-Band)	Dioxane	304	4250	304	4250	304	4250	304	4250	304	4250
	75% aqueous Dioxane	302-3	4000			302-3	4000	302	3900	301-2	3900
	50% aqueous Dioxane	301	3600	300	3500	300	3500	297-8	3500	296-7	3400
	25% aqueous Dioxane	297-8	3500	295	3500	295	3500	295	3500	294	3500
	Water	295-6	3500	294-5	3500	294	3500	294	3600	293-4	3700
o-Aminoacetophenone (B-Band)	Dioxane	253-4	5700	254	5600	254	5000	254	4700	255	3100
	75% aqueous Dioxane	254-5	5900	255	5800	255	5600	255	5100	255	4800
	50% aqueous Dioxane	255	5700	255	5700	255	5700	255	5700	255	5700
	25% aqueous Dioxane	255	5800	255	6000	258	5800	255	5800	255	5900
	Water	254-5	5800	254	6100	254-5	5900	254-5	5900	254-5	6200

Salicylic acid (C-Band)	50% aqueous Dioxane	301	3600	300	3500	300	3500	297-8	3500	296-7	3400
	25% aqueous Dioxane	297-8	3500	295	3500	295	3500	295	3500	294	3500
	Water	295-6	3500	294-5	3500	294	3500	294	3600	293-4	3700
o-Aminoacetophenone (B-Band)	Dioxane	253-4	5700	254	5600	254	5000	254	4700	255	3100
	75% aqueous Dioxane	254-5	5900	255	5800	255	5600	255	5100	255	4800
	50% aqueous Dioxane	255	5700	255	5700	255	5700	255	5700	255	5700
	25% aqueous Dioxane	255	5800	255	6000	258	5800	255	5800	255	5900
	Water	254-5	5800	254	6100	254-5	5900	254-5	5900	254-5	6200
o-Aminoacetophenone (C-Band)	Dioxane	354-5	4500	354-5	4500	354	4500	355	4500	354	4500
	75% aqueous Dioxane	356	4600	358	4500	358-9	4600	358	4500	357-8	4600
	50% aqueous Dioxane	357-8	4200	358	4200	358	4200	358	4200	357-8	4200
	25% aqueous Dioxane	357-8	3800	357	3900	358	3800	356-7	3800	356-7	3800
	Water	349	3500	349	3600	350	3500	350	3500	350	3600
Aniline (B-Band)	Cyclohexane	233	9000			233-4	9000	234	9000	234	8000
	Ethanol[1]	234-5	5700	234	4000	234	1700	237	300	234	300
Aniline (C-Band)	Cyclohexane	286	1900	286	1800	286	1800	286	1750	286	1700
	Ethanol	285	1000	284	900	284	900	284	600	284	500

[1] See experimental.